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**Synthesis and characterization of gallium-arsenic compounds  
containing a four-membered  $\overline{\text{Ga-As-Ga-Cl}}$  or  $\overline{\text{Ga-As-Ga-As}}$  ring:  
crystal structures of  $(\text{Me}_3\text{SiCH}_2)_2\overline{\text{GaAs(SiMe}_3)_2\text{Ga(CH}_2\text{SiMe}_3)_2\text{Cl}}$   
and  $[(\text{Me}_3\text{SiCH}_2)_2\overline{\text{GaAs(SiMe}_3)_2}]_2$**

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James D. Johansen, and Abbas Alvanipour**

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Durham, NC 27706 (U.S.A.)*

**Abstract**

The third example of an organogallium four-membered ring compound with arsenic, halogen mixed bridging,  $(\text{Me}_3\text{SiCH}_2)_2\overline{\text{GaAs(SiMe}_3)_2\text{Ga(CH}_2\text{SiMe}_3)_2\text{Cl}}$  (**1**), was prepared by the reaction of  $(\text{Me}_3\text{Si})_3\text{As}$  (**2**) with two equivalents of  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCl}$ . X-ray crystallographic analysis showed that the compound contains a nonplanar  $\overline{\text{Ga-As-Ga-Cl}}$  ring. The crystals belong to the monoclinic system space group  $P2_1/c$  ( $C^5_2h$ ) with four molecules per unit cell of dimensions  $a$  12.476(2),  $b$  15.832(2),  $c$  22.279(3) Å,  $\beta$  108.87(1)°,  $V$  4164(2) Å<sup>3</sup>. The dimer  $[(\text{Me}_3\text{SiCH}_2)_2\overline{\text{GaAs(SiMe}_3)_2}]_2$  (**3**) was prepared by reaction of  $\text{LiAs(SiMe}_3)_2$  and  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCl}$ . Its solid-state dimeric structure was established by single-crystal X-ray analysis. Crystals of **3** belong to the orthorhombic system space group  $Pbcn$  ( $D^{14}_2h$ ) with four dimers in a unit cell of dimensions  $a$  12.886(1),  $b$  21.172(2),  $c$  18.610(2) Å,  $V$  5077(1) Å<sup>3</sup>. The centrosymmetric dimers contain a planar  $\overline{\text{Ga-As-Ga-As}}$  ring with Ga-As bond lengths of 2.572(1) and 2.561(1) Å, and As-Ga-As angles of 85.85(3) and 86.32(3), and a Ga-As-Ga 93.91(2)°. Compound **3** reacts with two equivalents of  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCl}$  to produce **1** as a minor product along with a mixture of other unidentified products. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the product mixture obtained from the reaction of **3** with two equivalents of  $\text{Ph}_2\text{GaCl}$  and that from the reaction of  $[\text{Ph}_2\text{GaAs(SiMe}_3)_2]_2$  with two equivalents of  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCl}$  display some common signals, which are believed to be due to  $\text{Ph}_2\overline{\text{GaAs(SiMe}_3)_2\text{Ga(CH}_2\text{SiMe}_3)_2\text{Cl}}$ .

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SYNTHESIS AND CHARACTERIZATION OF GALLIUM-ARSENIC COMPOUNDS  
CONTAINING A FOUR-MEMBERED Ga-As-Ga-Cl OR Ga-As-Ga-As RING: CRYSTAL  
STRUCTURES OF  $(\text{Me}_3\text{SiCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$  AND  
 $[(\text{Me}_3\text{SiCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$

by

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## Synthesis and characterization of gallium-arsenic compounds

containing a four-membered Ga-As-Ga-Cl or Ga-As-Ga-As ring:

crystal structures of  $(\text{Me}_3\text{SiCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$   
and  $[(\text{Me}_3\text{SiCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$

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*(Received September 18, 1990)*

### Abstract

The third example of an organogallium four-membered ring compound with arsenic, halogen mixed bridging,  $(\text{Me}_3\text{SiCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$  (**1**), was prepared by the reaction of  $(\text{Me}_3\text{Si})_3\text{As}$  (**2**) with two equivalents of  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCl}$ . X-ray crystallographic analysis showed that the compound contains a nonplanar Ga-As-Ga-Cl ring. The crystals belong to the monoclinic system space group  $P2_1/c$  ( $C^5_2h$ ) with four molecules per unit cell of dimensions  $a$  12.476(2),  $b$  15.832(2),  $c$  22.279(3) Å,  $\beta$  108.87(1)°,  $V$  4164(2) Å<sup>3</sup>. The dimer  $[(\text{Me}_3\text{SiCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (**3**) was prepared by reaction of  $\text{LiAs}(\text{SiMe}_3)_2$  and

(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>GaCl. Its solid-state dimeric structure was established by single-crystal X-ray analysis. Crystals of **3** belong to the orthorhombic system space group *Pbcn* (*D*<sup>14</sup><sub>2h</sub>) with four dimers in a unit cell of dimensions *a* 12.886(1), *b* 21.172(2), *c* 18.610(2) Å, *V* 5077(1) Å<sup>3</sup>. The centrosymmetric dimers contain a planar Ga-As-Ga-As ring with Ga-As bond lengths of 2.572(1) and 2.561(1) Å, and As-Ga-As angles of 85.85(3) and 86.32(3), and a Ga-As-Ga 93.91(2)°. Compound **3** reacts with two equivalents of (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>GaCl to produce **1** as a minor product along with a mixture of other unidentified products. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the product mixture obtained from the reaction of **3** with two equivalents of Ph<sub>2</sub>GaCl and that from the reaction of [Ph<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> with two equivalents of (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>GaCl display some common signals, which are believed to be due to Ph<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>Ga(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>Cl.

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## Introduction

As part of our continuing investigations on the synthesis of arsinogallanes via dehalosilylation between a silylarsine and a halogallane [1, 2], or by coupling reactions between a lithium arsenide and a chlorogallane [3, 4], we have recently reported that the reactions of (Me<sub>3</sub>Si)<sub>3</sub>As (**2**) with Ph<sub>2</sub>GaCl and Ph<sub>2</sub>GaBr produce unprecedented four-membered ring compounds of the form Ph<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>Ga(Ph)<sub>2</sub>X [X = Cl (**4**), Br (**5**)] [5]. To investigate further the generality of this behavior, we have extended our studies to include a halogallane bearing a bulkier group. The reaction of (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>GaCl with **2** has been found to follow the same route producing a similar mixed bridge compound (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>Ga(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>Cl (**1**). We have also investigated the reaction between LiAs(SiMe<sub>3</sub>)<sub>2</sub> and (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>GaCl. A dimeric compound, [(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>Ga-As(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**3**), similar to the previously reported [Ph<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> [5], was obtained. We now report the complete characterization of compounds **1** and **3**, including their crystal structures, as well as some reactivity studies of **3**.

## Experimental

### General Comments

All manipulations and reactions were performed *in vacuo* or under an atmosphere of argon in a Vacuum/Atmospheres HE-43 Dri-Lab, or under an atmosphere of N<sub>2</sub> in standard Schlenk apparatus. Solvents were distilled from sodium benzophenone ketyl under nitrogen and degassed by several freeze-pump-thaw cycles. [Ph<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, Ph<sub>2</sub>GaCl [5a], (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>GaCl [6], (Me<sub>3</sub>Si)<sub>3</sub>As (2), and LiAs(SiMe<sub>3</sub>)<sub>2</sub>·2THF [7] were prepared by published methods. <sup>1</sup>H (299.943 MHz) and <sup>13</sup>C{<sup>1</sup>H} (75.429 MHz) NMR spectra were recorded on a Varian XL-300 spectrometer in C<sub>6</sub>D<sub>6</sub> solution. Chemical shifts are reported versus C<sub>6</sub>D<sub>5</sub>H δ 7.15 ppm and C<sub>6</sub>D<sub>6</sub> δ 128.0 ppm for <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR, respectively. Melting points (uncorrected) were obtained in sealed capillaries on a Mel-Temp apparatus. Elemental analyses were performed by E + R Microanalytical Laboratory, Corona, NY.

### Reaction of (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>GaCl with (Me<sub>3</sub>Si)<sub>3</sub>As (2) (1:1 mole ratio)

Bis(trimethylsilylmethyl)gallium chloride (0.558 g, 2.00 mmol) in 40 mL of benzene and 2 (0.590 g, 2.00 mmol) in 5 mL of C<sub>6</sub>H<sub>6</sub> were combined in a 100 mL one-necked round-bottom flask equipped with a Teflon valve and a stirbar. The flask contents were freeze-pump-thawed once and left to stir for 5 days at room temperature. Subsequent removal of the volatiles *in vacuo* afforded a semi-solid material. The crude product was dissolved in a small amount of pentane and cooled to -15 °C for 24 h to give 1 as colorless crystals suitable for single-crystal X-ray analysis (0.39 g, 51% yield based on gallium); m.p. 65-75 °C, becoming yellow at 120 °C and finally red at 160 °C. Analysis found for C<sub>22</sub>H<sub>62</sub>AsClGa<sub>2</sub>Si<sub>6</sub> (calcd): C, 35.67 (35.49), H, 8.21 (8.33). <sup>1</sup>H NMR: δ 0.26 (s, 18 H, SiMe<sub>3</sub>), 0.38 (s, 44 H, CH<sub>2</sub>SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 2.59 (SiMe<sub>3</sub>), 4.10 (SiMe<sub>3</sub>), 8.97 (CH<sub>2</sub>).

*Reaction of (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>GaCl with (Me<sub>3</sub>Si)<sub>3</sub>As (2) (2:1 mole ratio)*

Bis(trimethylsilylmethyl)gallium chloride (0.558 g, 2.00 mmol) in 40 mL of benzene and **2** (0.295 g, 1.00 mmol) in 5 mL of C<sub>6</sub>H<sub>6</sub> were combined in a 100 mL one-necked round-bottom flask equipped with a Teflon valve and a stirbar. The flask contents were freeze-pump-thawed once, allowed to stir for 5 days at room temperature and worked up as above. The crude semi-solid was dissolved in a small amount of pentane and cooled to -15 °C to give **1** as colorless crystals (0.43 g, 58% yield based on arsenic); m.p. 65-75 °C. Analysis found for C<sub>22</sub>H<sub>62</sub>AsClGa<sub>2</sub>Si<sub>6</sub> (calcd): C, 35.21 (35.49), H, 8.50 (8.33). <sup>1</sup>H NMR: δ 0.27 (s, 18 H, SiMe<sub>3</sub>), 0.39 (s, 44 H, CH<sub>2</sub>SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 2.58 (SiMe<sub>3</sub>), 4.10 (SiMe<sub>3</sub>), 8.97 (CH<sub>2</sub>).

*Preparation of [(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (3)*

To a solution of (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>GaCl (0.292 g, 1.00 mmol) in 30 mL of C<sub>6</sub>H<sub>6</sub> was added LiAs(SiMe<sub>3</sub>)<sub>2</sub>·2THF (0.35 g, 0.94 mmol) in 25 mL of C<sub>6</sub>H<sub>6</sub>. Stirring at room temperature for 30 h followed by removal of solvent *in vacuo* afforded a tacky solid. Pentane was then vacuum transferred onto the solid and the LiCl precipitate was filtered through a fine frit. Removal of pentane *in vacuo* afforded a mixture of a white solid and a yellow oil. This mixture was redissolved in 3 mL of pentane and placed in a -15 °C freezer overnight to give colorless crystals suitable for single-crystal X-ray analysis (0.24 g, 52% yield) of **3**. Mp 145-165 °C (dec). Analysis found for C<sub>28</sub>H<sub>80</sub>Ga<sub>2</sub>As<sub>2</sub>Si<sub>8</sub> (calcd): C, 36.39 (36.13); H, 8.88 (8.60). <sup>1</sup>H NMR: δ 0.35 (s, 36 H, SiMe<sub>3</sub>), 0.37 (s, 8 H, CH<sub>2</sub>), 0.54 (s, 36 H, SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 3.46 (SiMe<sub>3</sub>), 5.27 (SiMe<sub>3</sub>); the <sup>13</sup>C methylene resonance was not observed.

*Reaction of 3 with (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>GaCl*

Bis(trimethylsilylmethyl)gallium chloride (6 mg, 0.02 mmol) and **3** (10 mg, 0.01 mmol) were combined in an NMR tube into which was vacuum transferred 1.5 mL of C<sub>6</sub>D<sub>6</sub>. The contents of the tube were then frozen in liquid nitrogen, the tube flame sealed, and the contents

thawed.  $^1\text{H}$  NMR spectra recorded after 10 and 24 h at room temperature and an additional 12 h at 50 °C were all identical, showing low intensity signals at 0.24 and 0.41 ppm corresponding to the mixed-bridge compound **1**, and several other signals arising from unidentified by-products.  $^{13}\text{C}\{^1\text{H}\}$  NMR also indicated the presence of **1**. No NMR signals corresponding to those due to the starting materials were observed.

#### *Reaction of 3 with $\text{Ph}_2\text{GaCl}$*

Diphenylgallium chloride (12 mg,  $4.6 \times 10^{-2}$  mmol) and **3** (22 mg,  $2.3 \times 10^{-2}$  mmol) were dissolved in *ca.* 0.5 mL of  $\text{C}_6\text{D}_6$  in an NMR tube following which the tube contents were frozen in liquid nitrogen and then the tube was flame sealed under vacuum and its contents thawed.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the sample were obtained daily as the reaction was allowed to proceed for one week at room temperature and then at 53 °C for 42 h. The signals corresponding to the starting materials disappeared within 1 h of preparing the sample, and the new signals remained essentially unchanged during the subsequent reaction and heating steps.  $^1\text{H}$  NMR:  $\delta$  0.230 (s), 0.240 (s), 0.246 (s), 0.327 (s), 0.373 (s), 7.233 (complex doublet of triplets), 7.331 (complex triplet), 7.866 (complex doublet), 7.972 (broad multiplet), plus other minor peaks in the silyl region.  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  2.10, 2.48, 2.53, 3.25, 3.40, 3.50, 6.05, 6.53, 9.11, 135.09, 135.23, 135.81, 135.90, 149.28.

#### *Reaction of $[\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2]_2$ with $(\text{Me}_3\text{SiCH}_2)_2\text{GaCl}$*

Bis(trimethylsilylmethyl)gallium chloride (9.0 mg,  $3.2 \times 10^{-2}$  mmol) and  $[\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (14.3 mg,  $1.6 \times 10^{-2}$  mmol) were dissolved in *ca.* 0.5 mL of  $\text{C}_6\text{D}_6$  in an NMR tube following which the tube contents were frozen in liquid nitrogen and then the tube was flame sealed under vacuum and its contents thawed.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the sample were obtained daily as the reaction was allowed to proceed for one week at room temperature and then at 53 °C for 40 h. The signals corresponding to the starting materials disappeared within 1 h of preparing the sample. NMR data before heating the sample follow:  $^1\text{H}$  NMR:  $\delta$  0.146 (s),



0.199 (s), 0.220 (s), 0.235 (s), 0.898 (broad singlet), 1.353 (broad singlet), 3.250 (broad singlet), 7.259 (complex doublet), 7.331 (complex triplet), 7.963 (broad singlet), plus other minor peaks in the silyl region.  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  2.10, 2.40, 2.46, 2.53, 2.98, 3.12, 135.09, 135.22, 137.70 (broad), 145.34. NMR data after heating the sample follow:  $^1\text{H}$  NMR:  $\delta$  0.116 (s), 0.149 (s), 0.155 (s), 0.157 (s), 0.172 (s), 0.259 (s), 0.870 (broad singlet), 1.340 (broad singlet), 3.20 (broad singlet), 7.140 (multiplet), 7.245 (multiplet), 7.331 (complex triplet), 7.776 (complex doublet), 7.881 (broad singlet), 7.905 (broad singlet), plus other minor peaks in the silyl region.  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  2.06, 2.11, 2.43, 2.48, 2.55, 2.95, 3.00, 3.23, 3.28, 3.38, 6.10, 6.50, 9.10, 12.78, 135.06, 135.11, 135.19, 135.24, 137.66 (broad).

#### *X-ray crystal structure analysis of 1 and 3*

**Crystal data.**  $\text{C}_{22}\text{H}_{62}\text{AsClGa}_2\text{Si}_6$  (**1**),  $M$  745.07, monoclinic,  $a$  12.476(2),  $b$  15.832(3),  $c$  22.279(3) Å,  $\beta$  108.87(1) $^\circ$  (from 25 orientation reflections,  $42^\circ < \theta < 48^\circ$ ),  $V$  4164(2) Å<sup>3</sup>,  $Z$  = 4,  $D_c$  1.188 g cm<sup>-3</sup>,  $\mu(\text{Cu-K}\alpha)$  radiation ( $\lambda$  1.5418 Å) 48.4 cm<sup>-1</sup>; space group  $P2_1/c$  ( $C^5_2h$ ) uniquely from the systematic absences:  $0k0$  when  $k \neq 2n$ ,  $h0l$  when  $l \neq 2n$ ; crystal dimensions 0.41 x 0.46 x 0.46 mm.  $\text{C}_{28}\text{H}_{80}\text{As}_2\text{Ga}_2\text{Si}_8$  (**3**),  $M$  930.92, orthorhombic,  $a$  12.886(1),  $b$  21.172(2),  $c$  18.610(2) Å (from 25 orientation reflections,  $43^\circ < \theta < 48^\circ$ ),  $V$  5077(1) Å<sup>3</sup>,  $Z$  = 4,  $D_c$  1.218 g cm<sup>-3</sup>,  $\mu(\text{Cu-K}\alpha)$  radiation ( $\lambda$  1.5418 Å) 47.3 cm<sup>-1</sup>; space group  $Pbcn$  ( $D^{14}_2h$ ) uniquely from the systematic absences:  $0kl$  when  $k \neq 2n$ ,  $h0l$  when  $l \neq 2n$ ,  $hk0$  when  $h + k \neq 2n$ ; crystal dimensions 0.40 x 0.40 x 0.45 mm.

**Crystallographic measurements.** For X-ray data collection, crystals of **1** and **3** were sealed inside thin-walled glass capillaries. Intensity data to  $\theta_{\text{max}}$  75 $^\circ$  ( $+h,+k,\pm l$ , 8551 reflections for **1**;  $+h,+k,+l$ , 5228 reflections for **3**) were recorded at 25  $^\circ\text{C}$  on an Enraf Nonius CAD-4 diffractometer (Cu-K $\alpha$  radiation, graphite monochromator,  $\omega$ -2 $\theta$  scans; scanwidth:  $(1.00 + 0.14 \tan \theta)^\circ$  for **1**,  $(0.90 + 0.14 \tan \theta)^\circ$  for **3**. Equivalent reflections for **1** were averaged ( $R_{\text{merge}}$  0.029 on I) to yield 8345 unique measurements. Following corrections for Lorentz and polarization effects, absorption (empirical;  $T_{\text{max}}/T_{\text{min}}$ : 1.00/0.80 for **1**, 1.00/0.78 for **3**), and in

the case of **3** also linear decay (13%), those 5618 and 2987 reflections with  $I > 3.0\sigma(I)$  for **1** and **3**, respectively, were retained for the structural analysis.

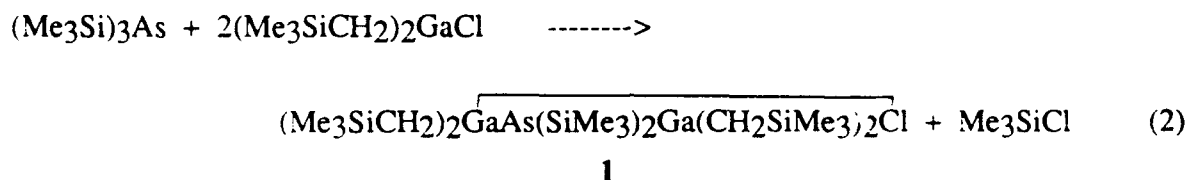
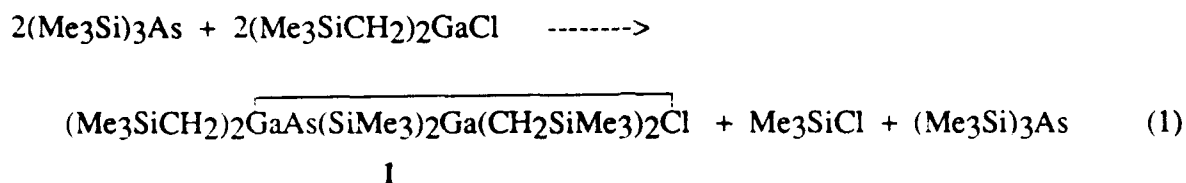
*Structural analysis.* Both crystal structures were solved by direct methods. With four formula units per unit cell, ordered molecules of **1** must occupy the general positions of space group  $P2_1/c$  since **1** lacks a center of symmetry. Initial non-hydrogen atom positions were obtained from an  $E$ -map. For **3**, the presence of only four formula units per unit cell demands that the molecule lies either on a crystallographic center of symmetry or on a two-fold axis of symmetry. Approximate non-hydrogen atom coordinates were derived in part from an  $E$ -map and from difference Fourier syntheses. Positional and thermal parameters (at first isotropic, then anisotropic) for the non-hydrogen atoms of **1** and **3** were adjusted by means of several cycles of full-matrix least-squares calculations during the final rounds of which hydrogen atoms were included at calculated positions and an extinction correction ( $g$ ) was varied. The parameter refinements converged (maximum shift/esd  $< 0.02$ ) at  $R = 0.046$  ( $R_w = 0.062$ , GOF 1.66,  $g$   $8.3(2) \times 10^{-7}$ ) [8] for **1** and  $R = 0.048$  ( $R_w = 0.065$ , GOF 1.31,  $g$   $4.8(1) \times 10^{-7}$ ) for **3**. Final non-hydrogen atom positional parameters for **1** and **3** are listed in Tables 1 and 2, respectively; ORTEP diagrams showing the solid-state conformations are provided in Figures 1 and 2. Bond lengths and angles involving the non-hydrogen atoms for **1** are in Table 3 while values for **3** are in Table 4. Selected torsion angles for both compounds are in Table 5; displacements of atoms from selected least-squares planes for are in Table 6. Tables of anisotropic temperature factor parameters, hydrogen atom parameters, torsion angles, and observed and calculated amplitudes are available from the authors (RLW).

Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP) incorporating the direct methods program MULTAN11/82. For structure factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from reference 9. For the least-squares iterations,  $\sum w \Delta^2$  [ $w = 1/\sigma^2(|F_O|)$ ,  $\Delta = (|F_O| - |F_C|)$ ] was minimized.

## Results and Discussion

The reactions of  $(\text{Me}_3\text{Si})_3\text{As}$  (**2**) with  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCl}$  in 1:1 and 1:2 mole ratio at room temperature in benzene yield the common product **1**, corresponding to elimination of one equivalent of  $\text{Me}_3\text{SiCl}$

per two equivalents of  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCl}$  (eqns. 1, 2). Presence of the  $\text{Me}_3\text{SiCl}$  by-products

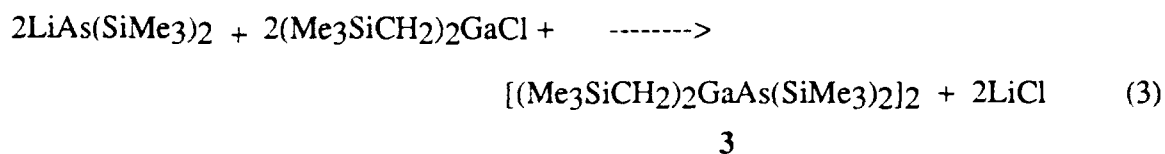


of both reactions as well as excess unreacted  $(\text{Me}_3\text{Si})_3\text{As}$  in the 1:1 reaction was confirmed by identification of their signals in the  $^1\text{H}$  NMR spectra of the reaction volatiles.

The  $^1\text{H}$  NMR spectrum of **1** shows only one type of trimethylsilyl and trimethylsilylmethyl group, with the methylene signals of the latter accidentally degenerate with its methyl signals. Based on the x-ray crystal structure of this compound (*vide infra*), two types of environments for each type of ligand are expected. It has been demonstrated in the bis-mixed-bridge compound  $\text{Ph}_2\text{GaCl}(\text{Ph})_2\text{Ga}(\text{Me}_3\text{Si})\text{As}(\text{CH}_2)_3\text{As}(\text{SiMe}_3)\text{Ga}(\text{Ph})_2\text{ClGaPh}_2$  that processes involving Ga-Cl or Ga-As bond cleavage followed by rotation about the opposite bond in the ring and bond reformation are slow [10], thus it may be expected that such processes which would result in equivalency of resonances for the two types of trimethylsilyl and trimethylsilylmethyl ligands of **1** would also be slow on the NMR time scale. A simple envelope-flapping mechanism could therefore be invoked to rationalize the unexpectedly simple  $^1\text{H}$  NMR spectrum of **1**.

This method of forming Ga-As bonds by  $\text{Me}_3\text{SiX}$  elimination has ample precedent [1, 2, 10, 11], and has previously resulted in similar mixed bridge compounds  $\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{Ph})_2\text{X}$  [ $\text{X} = \text{Cl}$  (4),  $\text{Br}$  (5)] [5]. Factors governing the extent of  $\text{Me}_3\text{SiX}$  elimination in such reactions are not certain, but they are believed to include the reaction stoichiometry, the temperature and duration of the reaction, and the electronic and steric natures of the various substituent groups on the gallium and arsenic centers. Although they have been implicated as intermediates in the formation of  $[\text{R}_2\text{GaAsR}'_2]_2$  type compounds [5b], mixed bridge compounds such as **1**, **4**, and **5** seem to be reasonably stable.

The reaction of  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCl}$  with  $\text{LiAs}(\text{SiMe}_3)_2 \cdot 2\text{THF}$  in a 1:1 ratio in benzene at room temperature yields the dimer  $[(\text{Me}_3\text{SiCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (**3**) (eqn. 3). The  $^1\text{H}$  NMR



spectrum of **3** is consistent with expectations based on its solid-state structure (*vide infra*) and remains invariant even after heating the sample to  $50^\circ\text{C}$  for 27 h, thus attesting to its remarkable stability.

The lithium chloride elimination route used in the present work has been used previously to form Ga-As bonds [3, 4, 12, 13] and, more importantly, in the synthesis of  $[\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  [5] in which  $\text{LiCl}$  elimination is the method of choice to produce the dimer cleanly. A number of other  $(\text{Ga-As})_2$  dimeric compounds are known [14], some of which are listed in Table 7.

The detailed structures of **1** and **3** were established by X-ray crystallography. Bond lengths and angles for **1** and **3** are given in Tables 3 and 4, respectively. ORTEP diagrams of **1** and **3** are presented in Figures 1 and 2, respectively.

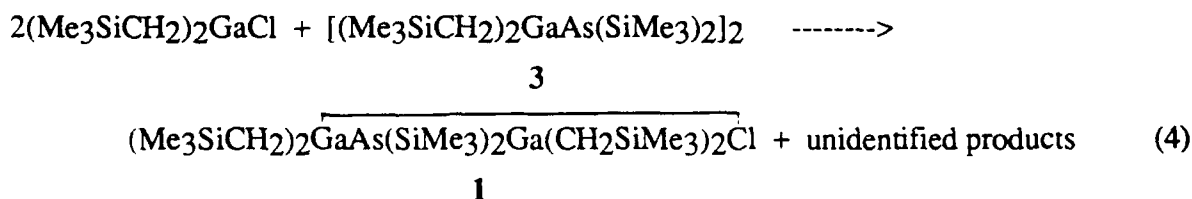
The unit cell of **1** contains four molecules which occupy the general positions of centrosymmetric space group  $P2_1/c$  and are separated by normal van der Waals distances. In **1**, the  $\text{Ga-As-Ga'-Cl}$  ring geometry is similar to that in analog **4** [5] which has phenyl groups at the

Ga atoms instead of  $\text{Me}_3\text{SiCH}_2$  substituents. The Cl atom displacement of  $0.860 \text{ \AA}$  from the Ga-As-Ga' plane in **1** and the associated dihedral angle between the Ga-As-Ga' and Ga-Cl-Ga' planes at  $30.40(6)^\circ$  reflect a much greater degree of ring puckering than that found in **4** where the corresponding values are  $0.256 \text{ \AA}$  and  $8.8(2)^\circ$ . Ring puckering in these compounds occurs in a manner which serves to relieve substituent overcrowding. Thus, outward rotation of a pair of Ga-C bond vectors on one face of the ring in **1** and **4** with concomitant displacement of the Cl atom from the Ga-As-Ga' plane produces ring puckering. Departure from exact  $C_s$  molecular symmetry wherein a mirror plane bisects the As and Cl atoms is evident from the non-orthogonal relationship of the Ga-As-Ga' and Si-As-Si' planes [dihedral angle =  $84.51(4)^\circ$ ] in addition to the slightly different Ga-Cl bond distances [ $2.437(1)$ ,  $2.426(1) \text{ \AA}$ ] of which the longer involves the Ga atom towards which the proximal  $\text{Me}_3\text{Si}$  group is rotated. Ga-As and Ga-Cl bond lengths in **1** are longer than corresponding values in **4**. In common with **4**, however, the endocyclic bond angles at Ga and As in **1** fall within a narrow range ( $86.26(3) - 87.96(2)^\circ$ ). The Ga-Cl-Ga' angle in **1** [ $91.33(4)^\circ$ ] is virtually identical with that in **4** [ $91.3(1)^\circ$ ] as well as that of  $91.4(4)^\circ$  in  $[(\text{C}_5\text{Me}_5)\text{GaCl}(\mu\text{-Cl})_2]$  [15], and it lies intermediate between those of  $86(2)^\circ$  in  $(\text{GaCl}_3)_2$  [16], and  $97.2(3)^\circ$  and  $97.5(2)^\circ$  in  $[(\text{C}_5\text{Me}_5)_2\text{Ga}(\mu\text{-Cl})_2]$  [145]. The mean exocyclic C-Ga-C' angle in **1** at  $123.6(2)^\circ$  is slightly larger than the means in **4** ( $121.3(5)^\circ$ ) and  $[\text{Ph}_2\text{GaAs}(\text{CH}_2\text{SiMe}_3)_2]_2$  [ $120.8(2)^\circ$ ] [17], while the Si-As-Si' angle at  $108.64(6)^\circ$  in **1** is intermediate between those of  $111.0(2)^\circ$  and  $103.2(4)^\circ$  in **4** and  $[(\text{Me}_3\text{Si})_2\text{AsLi-DME}]_2$  [18], respectively.

Compound **3** crystallizes in the centrosymmetric space group  $Pbcn$  with only four formula units per unit cell, and thus the molecule must possess either  $C_i$  or  $C_2$  symmetry. Solution of the crystal structure revealed that the Ga atoms lay on a crystallographic  $C_2$  axis of symmetry. The planar four-membered  $\overline{\text{Ga-As-Ga'-As'}}$  ring is characterized by slightly unequal Ga-As bond lengths [ $2.572(1)$ ,  $2.561(1) \text{ \AA}$ ], a Ga-As-Ga' angle of  $93.91(2)^\circ$ , and As-Ga-As angles of  $88.85(3)$  and  $86.32(3)^\circ$ , and, accordingly, it deviates from a strictly square planar geometry. Structural parameters derived from X-ray crystallographic studies of  $\overline{\text{Ga-As-Ga'-As'}}$  rings in several compounds are summarized in Table 7. The mean of the Ga-As bonded distances in **1** ( $2.567 \text{ \AA}$ )

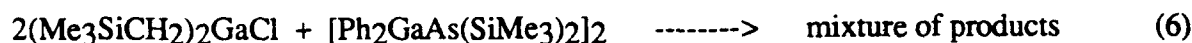
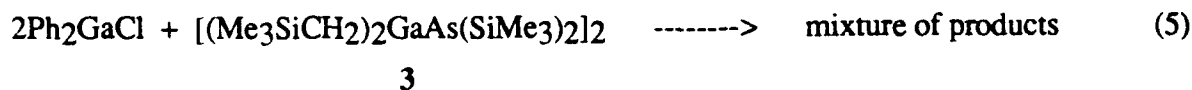
lies close to those of 2.555 Å in  $\{\text{Ga}[\text{As}(\text{CH}_2\text{SiMe}_3)_2]_3\}_2$  [4] and 2.550 Å in  $(\text{Me}_2\text{GaAsBu}^t)_2$  [19] but it is significantly longer than those at 2.517 Å in  $\{\text{BrGa}[\text{As}(\text{CH}_2\text{SiMe}_3)_2]_2\}_2$  [2] and 2.524 Å in  $[\text{Ph}_2\text{GaAs}(\text{CH}_2\text{SiMe}_3)_2]_2$  [17]. A consistent feature of all compounds listed in Table 7 is the obtuse nature of the Ga-As-Ga ring angle (which requires that the As-Ga-As ring angle is always acute). Exocyclic bond angles subtended at As and Ga in **1** ( $\text{Si-As-Si} = 103.66(6)^\circ \ll \text{C-Ga-C} = 123.2(3), 124.6(3)^\circ$ ) are typical for this class of compound. Of those representative examples listed in Table 7,  $\{\text{Ga}[\text{As}(\text{CH}_2\text{SiMe}_3)_2]_3\}_2$  has a nonplanar  $\overline{\text{Ga-As-Ga-As}}$  core, and thus there seems to be no general preference for a planar ring geometry. The actual geometry adopted by this type of compound appears to be dependent to a considerable extent upon intramolecular interligand repulsions which, if sufficiently great, can lead to the existence of Ga-As monomers as exemplified by  $\text{Bu}^t_2\text{GaAsBu}^t_2$  [12] and  $(\text{C}_5\text{Me}_5)_2\text{GaAs}(\text{SiMe}_3)_2$  [13].

It has been reported that  $[\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  reacts with two equivalents of  $\text{Ph}_2\text{GaCl}$  cleanly to afford  $\text{Ph}_2\overline{\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{Ph})_2}\text{Cl}$  (**4**) [5]. Likewise, **3** reacts with two equivalents of  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCl}$  to afford **1**, though in this case the mixed-bridge product is only one of a number of products (eqn. 4). The reaction depicted in eqn. 4 is complete within 12 h at room



temperature. Although both starting materials are completely consumed according to the  $^1\text{H}$  NMR spectrum of the sample, it may have been expected based on the precedent of the analogous **4** that this route to **1** would have been quantitative. Even though this is not the case, it is significant that the principle of the preparation of a gallium-arsenic mixed-bridge compound using a gallium-arsenic dimer and a dialkylgallium halide has been further extended.

In an effort to explore further this method of preparing gallium-arsenic mixed-bridge compounds, the reactions depicted in equations 5 and 6 were performed in sealed NMR tubes and monitored by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy. In both cases complete disappearance of the



starting materials was observed within one hour of preparing the samples, and in neither reaction were the starting materials for the complementary reaction observed.

In the hypothetical compound  $\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ , if the structure was similar to **1** and an envelope-flapping mechanism was operating in which the chlorine atom was in a time-averaged position in the Ga-As-Ga plane, giving the molecule idealized  $\text{C}_s$  symmetry, in the  $^1\text{H}$  NMR spectrum we could expect to observe one set of phenyl resonances, two silyl methyl resonances, and a silyl methylene AA'BB' pattern, while in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum we should observe three silyl resonances and four phenyl resonances. Both the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of both reaction mixtures are considerably more complicated than what would be expected of the hypothetical compound above, but the likelihood of side reactions is high, as exemplified in the preparation of **1** from **3** and  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCl}$  (*vide supra*). In addition, the precedent exists in **1** for overlapping  $\text{CH}_2$  and  $\text{CH}_3$  resonances in the  $\text{Me}_3\text{SiCH}_2\text{Ga}$  moiety, which may be occurring here though the expected AA'BB' methylene proton pattern may merely be obscured by the baseline clutter in the silyl region of both  $^1\text{H}$  NMR spectra. Nevertheless, there are many common resonances observed in the NMR spectra of reactions 5 and 6, indicating the presence of common products, possibly including the hypothesized product  $\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ . Significantly, several phenyl multiplets in the  $^1\text{H}$  NMR spectra of reactions 5 and 6 are of identical shape and also closely resemble the phenyl multiplets observed for  $[\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  and **4** [5], suggesting similar magnetic environments and thus

molecular structures. Thus, while the available data are not conclusive, they nevertheless suggest that reactions 5 and 6 give a common product believed to be  $\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ . It is noteworthy that reaction 5 appears to be cleaner than reaction 6, and use of a different alkyl group on the gallium atoms also may unambiguously and successfully yield a desired gallium-arsenic hybrid mixed-bridge compound.

### Acknowledgement

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## References

- 1 C.G. Pitt, A.P. Purdy, K.T. Higa, and R.L. Wells, *Organometallics*, 5 (1986) 1266.
- 2 A.P. Purdy, R.L. Wells, A.T. McPhail, and C.G. Pitt, *Organometallics*, 6 (1987) 2099.
- 3 C.G. Pitt, K.T. Higa, A.T. McPhail, and R.L. Wells, *Inorg. Chem.*, 25 (1986) 2483.
- 4 R.L. Wells, A.P. Purdy, K.T. Higa, A.T. McPhail, and C.G. Pitt, *J. Organomet. Chem.*, 325 (1987) C7.
- 5 (a) W.K. Holley, R.L. Wells, S. Shafieezad, A.T. McPhail, and C.G. Pitt, *J. Organomet. Chem.*, 381 (1990) 15. (b) R.L. Wells, W.K. Holley, S. Shafieezad, A.T. McPhail, and C.G. Pitt, *Phosphorus, Sulfur, Silicon, Relat. Elem.*, 41 (1989) 15.
- 6 O.T. Beachley, Jr. and J.C. Pazik, *Organometallics*, 7 (1988) 1516.
- 7 G. Becker, G. Gutekunst, and H.J. Wessely, *Z. anorg. allg. Chem.*, 462 (1980) 113.
- 8  $R = \Sigma ||F_O| - |F_C|| / \Sigma |F_O|$ ;  $R_W = [\Sigma w(|F_O| - |F_C|)^2 / \Sigma w|F_O|^2]^{1/2}$ ; GOF (Goodness-Of-Fit) =  $[\Sigma w\Delta^2 / (N_{\text{observations}} - N_{\text{parameters}})]^{1/2}$ .
- 9 *International Tables for X-Ray Crystallography*, vol. IV, The Kynoch Press, Birmingham, England, 1974.
- 10 W.K. Holley, J.W. Pasterczyk, C.G. Pitt, and R.L. Wells, *Heteroatom Chem.*, in press.
- 11 R.L. Wells, C.G. Pitt, A.T. McPhail, A.P. Purdy, S. Shafieezad, and R.B. Hallock, *Chem. Mater.*, 1 (1989) 4.
- 12 K.T. Higa and C. George, *Organometallics*, 9 (1990) 275.
- 13 E.K. Byrne, L. Parkanyi, and K.H. Theopold, *Science*, 241 (1988) 332.
- 14 A.H. Cowley and R. A. Jones, *Angew. Chem. Int. Ed. Engl.*, 28 (1989) 1208.
- 15 O.T. Beachley, Jr., R.B. Hallock, H.M. Zhang, and J.L. Atwood, *Organometallics*, 4 (1985) 1675.
- 16 S.C. Wallwork and I.J. Worrall, *J. Chem. Soc.*, (1965) 1816.
- 17 R.L. Wells, A.P. Purdy, A.T. McPhail, and C.G. Pitt, *J. Organomet. Chem.*, 308 (1986) 281.

- 18 G. Becker and C. Witthauer, *Z. anorg. allg. Chem.*, 492 (1982) 28.
- 19 A.M. Arif, B.L. Benac, A.H. Cowley, R. Geerts, R.A. Jones, K.B. Kidd, J.M. Power, and S.T. Schwab, *J. Chem. Soc., Chem. Commun.*, (1986) 1543.

### Captions to Figures

Figure 1. ORTEP diagram (40% probability thermal ellipsoids) of **1** showing the atom numbering scheme and solid-state conformation. Hydrogen atoms have been omitted for clarity.

Figure 2. ORTEP diagram (40% probability thermal ellipsoids) of **3** showing the atom numbering scheme and solid-state conformation. Hydrogen atoms have been omitted for clarity.



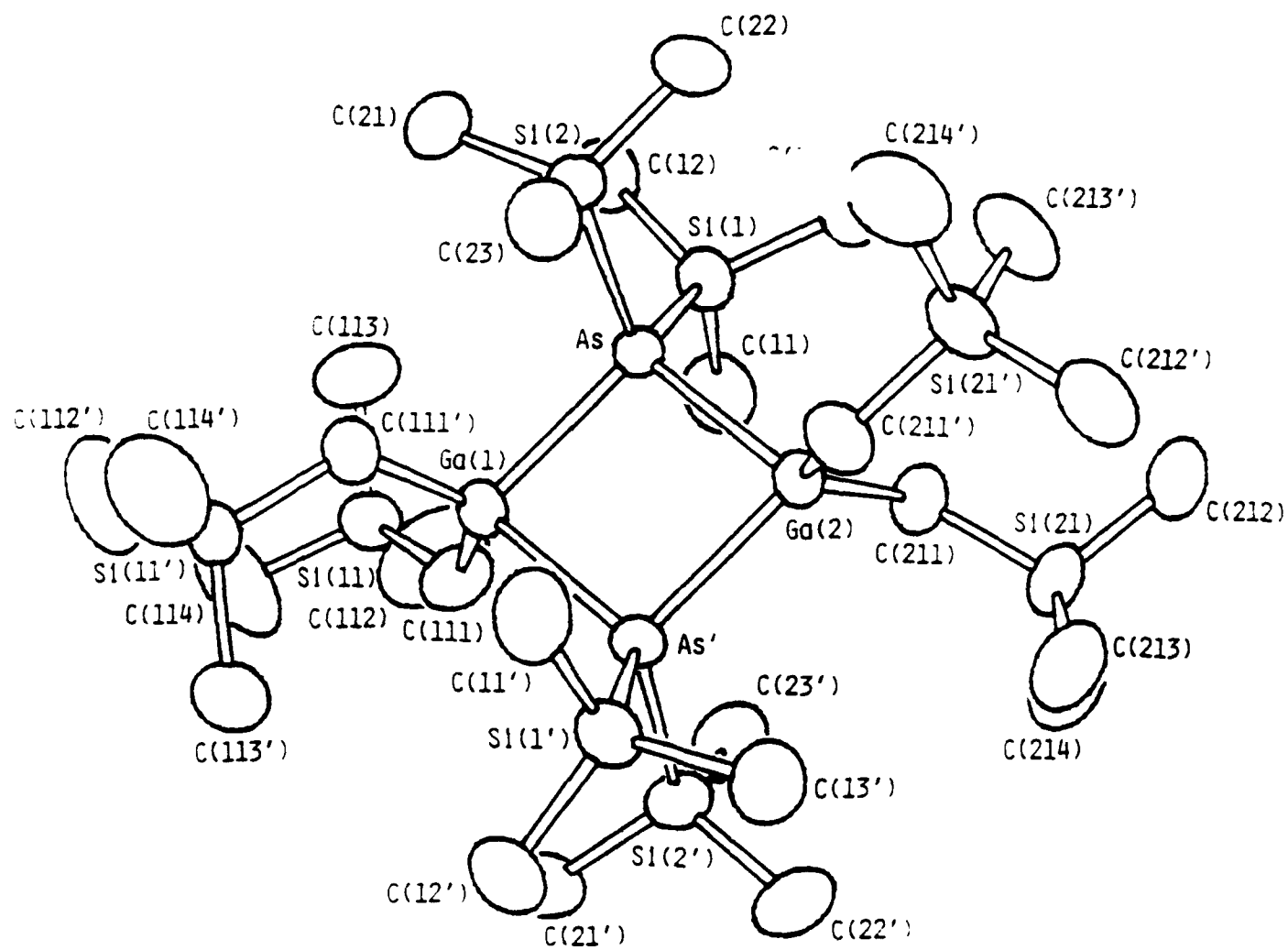


Figure 2

Table 1. Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters for 1, with estimated standard deviations in parentheses.

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$B_{eq}(\text{\AA}^2)$
As	0.18557(4)	0.21849(3)	-0.06706(2)	4.10(1)
Ga	0.29544(4)	0.22831(4)	0.04877(3)	4.20(1)
Ga'	0.03051(4)	0.29981(3)	-0.04480(2)	3.96(1)
Cl	0.17389(8)	0.34781(7)	0.05130(5)	4.75(2)
Si(1)	0.12802(12)	0.08618(9)	-0.11420(7)	5.28(3)
Si(2)	0.49557(11)	0.35369(11)	0.13753(7)	5.74(3)
Si(3)	0.35253(13)	0.04962(10)	0.12428(9)	6.36(4)
Si(1')	0.28490(11)	0.28934(12)	-0.12509(7)	6.38(4)
Si(2')	-0.13022(11)	0.26637(9)	0.04457(7)	5.29(3)
Si(3')	-0.14669(13)	0.39770(10)	-0.16741(7)	5.87(4)
C(11)	0.2504(5)	0.0336(4)	-0.1288(3)	7.7(2)
C(12)	0.0101(6)	0.1032(4)	-0.1899(3)	8.1(2)
C(13)	0.0751(5)	0.0215(4)	-0.0602(3)	6.9(2)
C(21)	0.4492(4)	0.2753(3)	0.0714(2)	5.3(1)
C(22)	0.6532(5)	0.3544(5)	0.1707(3)	8.7(2)
C(23)	0.4380(5)	0.3274(4)	0.2037(3)	7.1(2)
C(24)	0.4482(5)	0.4620(4)	0.1068(4)	8.6(2)
C(31)	0.2532(4)	0.1394(3)	0.0988(2)	5.2(1)
C(32)	0.2802(7)	-0.0449(5)	0.1431(4)	11.0(3)
C(33)	0.4742(6)	0.0780(5)	0.1948(4)	10.6(2)
C(34)	0.4095(5)	0.0172(5)	0.0588(4)	9.7(2)
C(11')	0.2119(6)	0.2810(6)	-0.2117(3)	11.1(2)
C(12')	0.4289(5)	0.2433(6)	-0.1069(3)	9.8(2)
C(13')	0.2948(6)	0.4007(5)	-0.0990(4)	10.8(2)
C(21')	-0.0641(4)	0.2237(3)	-0.0130(2)	4.5(1)
C(22')	-0.2603(4)	0.2052(5)	0.0382(3)	9.1(2)
C(23')	-0.1684(7)	0.3788(4)	0.0321(3)	12.2(2)
C(24')	-0.0300(7)	0.2533(7)	0.1262(3)	12.1(3)
C(31')	-0.0247(4)	0.4035(3)	-0.0927(2)	5.1(1)
C(32')	-0.1976(6)	0.5062(4)	-0.1923(3)	7.9(2)
C(33')	-0.2656(6)	0.3356(6)	-0.1581(4)	11.2(2)
C(34')	-0.1032(7)	0.3499(5)	-0.2314(3)	11.1(2)

Table 2. Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters for 3, with estimated standard deviations in parentheses.

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$B_{eq}(\text{\AA}^2)$
As	0.13491(4)	0.18420(3)	0.23851(3)	3.59(1)
Ga(1)	0.00000(-) <sup>a</sup>	0.27315(4)	0.25000(-) <sup>a</sup>	3.86(2)
Ga(2)	0.00000(-) <sup>a</sup>	0.09598(4)	0.25000(-) <sup>a</sup>	3.73(2)
Si(1)	0.2358(1)	0.17204(8)	0.1338(1)	4.92(3)
Si(2)	0.2592(1)	0.19022(8)	0.3312(1)	5.29(3)
Si(11)	0.0377(1)	0.38337(8)	0.1189(1)	5.13(3)
Si(21)	-0.0837(2)	-0.01874(8)	0.1361(1)	5.92(4)
C(11)	0.1515(7)	0.1869(4)	0.0554(4)	7.4(2)
C(12)	0.3482(6)	0.2283(4)	0.1327(5)	7.4(2)
C(13)	0.2877(6)	0.0901(3)	0.1285(4)	6.6(2)
C(21)	0.3277(6)	0.2677(4)	0.3285(5)	7.8(2)
C(22)	0.3595(6)	0.1266(4)	0.3197(5)	8.0(2)
C(23)	0.1927(7)	0.1821(4)	0.4195(4)	7.2(2)
C(111)	-0.0355(6)	0.3179(3)	0.1592(4)	6.2(1)
C(112)	0.0248(10)	0.3769(3)	0.0205(5)	13.6(4)
C(113)	0.1757(7)	0.3829(4)	0.1402(6)	9.9(3)
C(114)	-0.0169(9)	0.4584(5)	0.1472(10)	16.8(5)
C(211)	-0.0027(5)	0.0523(3)	0.1554(3)	5.2(1)
C(212)	0.0021(7)	-0.0888(4)	0.1219(6)	9.8(3)
C(213)	-0.1791(7)	-0.0363(4)	0.2098(5)	8.4(2)
C(214)	-0.1614(8)	-0.0069(5)	0.0514(5)	9.8(3)

<sup>a</sup>Fixed by symmetry.

Table 3. Bond lengths (Å) and angles (°) for 1, with estimated standard deviations in parentheses.

(a) Bond Lengths

As-Ga	2.505(1)	As-Ga'	2.503(1)
As-Si(1)	2.349(1)	As-Si(1')	2.346(2)
Ga-Cl	2.437(1)	Ga'-Cl	2.426(1)
Ga-C(21)	1.965(5)	Ga'-C(21')	1.972(5)
Ga-C(31)	1.970(5)	Ga'-C(31')	1.958(5)
Si(1)-C(11)	1.858(7)	Si(1')-C(11')	1.853(6)
Si(1)-C(12)	1.865(6)	Si(1')-C(12')	1.858(7)
Si(1)-C(13)	1.856(7)	Si(1')-C(13')	1.848(8)
Si(2)-C(21)	1.869(5)	Si(2')-C(21')	1.862(6)
Si(2)-C(22)	1.864(6)	Si(2')-C(22')	1.855(6)
Si(2)-C(23)	1.883(8)	Si(2')-C(23')	1.840(7)
Si(2)-C(24)	1.870(7)	Si(2')-C(24')	1.855(6)
Si(3)-C(31)	1.850(5)	Si(3')-C(31')	1.859(4)
Si(3)-C(32)	1.864(9)	Si(3')-C(32')	1.853(6)
Si(3)-C(33)	1.853(7)	Si(3')-C(33')	1.846(9)
Si(3)-C(34)	1.889(9)	Si(3')-C(34')	1.844(8)

(b) Bond Angles

Ga-As-Ga'	87.96(2)	Si(1)-As-Si(1')	108.64(6)
Ga-As-Si(1)	120.15(4)	Ga'-As-Si(1')	116.31(5)
Ga-As-Si(1')	109.12(4)	Ga'-As-Si(1)	113.77(4)
As-Ga-Cl	86.26(3)	As-Ga'-Cl	86.53(3)
As-Ga-C(21)	116.8(1)	As-Ga'-C(21')	110.3(1)
As-Ga-C(31)	112.4(1)	As-Ga'-C(31')	118.8(2)
Cl-Ga-C(21)	105.3(1)	Cl-Ga'-C(21')	103.3(1)
Cl-Ga-C(31)	105.0(2)	Cl-Ga'-C(31')	104.3(1)
C(21)-Ga-C(31)	122.9(2)	C(21')-Ga'-C(31')	124.2(2)
Ga-Cl-Ga'	91.33(4)		
As-Si(1)-C(11)	109.2(2)	As-Si(1')-C(11')	111.7(3)
As-Si(1)-C(12)	108.3(2)	As-Si(1')-C(12')	109.8(3)



Table 3. (continued)

As-Si(1)-C(13)	108.9(2)	As-Si(1')-C(13')	106.0(3)
C(11)-Si(1)-C(12)	111.0(3)	C(11')-Si(1')-C(12')	108.3(3)
C(11)-Si(1)-C(13)	110.5(3)	C(11')-Si(1')-C(13')	110.8(4)
C(12)-Si(1)-C(13)	108.9(3)	C(12')-Si(1')-C(13')	110.1(4)
C(21)-Si(2)-C(22)	109.5(3)	C(21')-Si(2')-C(22')	109.2(3)
C(21)-Si(2)-C(23)	111.8(3)	C(21')-Si(2')-C(23')	113.4(3)
C(21)-Si(2)-C(24)	109.9(3)	C(21')-Si(2')-C(24')	109.1(3)
C(22)-Si(2)-C(23)	108.2(3)	C(22')-Si(2')-C(23')	108.4(4)
C(22)-Si(2)-C(24)	107.9(3)	C(22')-Si(2')-C(24')	108.2(4)
C(23)-Si(2)-C(24)	109.5(3)	C(23')-Si(2')-C(24')	108.4(4)
C(31)-Si(3)-C(32)	111.2(3)	C(31')-Si(3')-C(32')	108.9(2)
C(31)-Si(3)-C(33)	111.0(3)	C(31')-Si(3')-C(33')	112.4(3)
C(31)-Si(3)-C(34)	110.7(3)	C(31')-Si(3')-C(34')	110.6(3)
C(32)-Si(3)-C(33)	109.1(4)	C(32')-Si(3')-C(33')	108.5(4)
C(32)-Si(3)-C(34)	106.6(4)	C(32')-Si(3')-C(34')	107.9(3)
C(33)-Si(3)-C(34)	108.1(3)	C(33')-Si(3')-C(34')	108.4(4)
Ga-C(21)-Si(2)	118.8(3)	Ga'-C(21')-Si(2')	118.4(2)
Ga-C(31)-Si(3)	116.6(3)	Ga'-C(31')-Si(3')	119.2(2)

Table 4. Bond lengths (Å) and angles (°) for 3, with estimated standard deviations in parentheses.

(a) Bond Lengths

As-Ga(1)	2.572(1)	Si(2)-C(22)	1.879(8)
As-Ga(2)	2.561(1)	Si(2)-C(23)	1.861(8)
As-Si(1)	2.357(2)	Si(11)-C(111)	1.837(7)
As-Si(2)	2.357(2)	Si(11)-C(112)	1.844(10)
Ga(1)-C(111)	1.991(7)	Si(11)-C(113)	1.822(9)
Ga(2)-C(211)	1.989(6)	Si(11)-C(114)	1.815(12)
Si(1)-C(11)	1.846(8)	Si(21)-C(211)	1.866(7)
Si(1)-C(12)	1.875(8)	Si(21)-C(212)	1.869(9)
Si(1)-C(13)	1.862(7)	Si(21)-C(213)	1.879(9)
Si(2)-C(21)	1.863(8)	Si(21)-C(214)	1.884(10)

(b) Bond Angles

Ga(1)-As-Ga(2)	93.91(2)	As-Si(2)-C(21)	110.5(3)
Ga(1)-As-Si(1)	121.44(5)	As-Si(2)-C(22)	110.2(3)
Ga(1)-As-Si(2)	111.03(5)	As-Si(2)-C(23)	109.2(3)
Ga(2)-As-Si(1)	111.34(5)	C(21)-Si(2)-C(22)	107.6(4)
Ga(2)-As-Si(2)	116.08(5)	C(21)-Si(2)-C(23)	108.9(4)
Si(1)-As-Si(2)	103.66(6)	C(22)-Si(2)-C(23)	110.6(4)
As-Ga(1)-C(111)	115.7(2)	C(111)-Si(11)-C(112)	107.6(5)
As-Ga(1)-As'	85.85(3)	C(111)-Si(11)-C(113)	114.1(4)
As-Ga(1)-C(111')	105.3(2)	C(111)-Si(11)-C(114)	110.1(5)
C(111)-Ga(1)-C(111')	123.2(3)	C(112)-Si(11)-C(113)	107.7(5)
As-Ga(2)-C(211)	106.1(2)	C(112)-Si(11)-C(114)	108.6(7)
As-Ga(2)-As'	86.32(3)	C(113)-Si(11)-C(114)	108.7(5)
As-Ga(2)-C(211')	113.7(2)	C(211)-Si(21)-C(212)	109.6(4)
C(211)-Ga(2)-C(211')	124.6(3)	C(211)-Si(21)-C(213)	112.6(3)
As-Si(1)-C(11)	108.1(3)	C(211)-Si(21)-C(214)	110.6(4)
As-Si(1)-C(12)	111.5(3)	C(212)-Si(21)-C(213)	109.5(4)
As-Si(1)-C(13)	110.1(2)	C(212)-Si(21)-C(214)	107.6(5)
C(11)-Si(1)-C(12)	109.7(4)	C(213)-Si(21)-C(214)	106.8(4)
C(11)-Si(1)-C(13)	109.2(4)	Ga(1)-C(111)-Si(11)	126.0(4)
C(12)-Si(1)-C(13)	108.3(3)	Ga(2)-C(211)-Si(21)	123.7(3)

Table 5. Selected torsion angles<sup>a</sup> (°) for 1 and 3, with estimated standard deviations in parentheses.

Compound 1

Ga'-As-Ga-Cl	-20.71(3)	Ga-As-Ga'-Cl	20.80(3)
Ga'-As-Ga-C(21)	-125.9(2)	Ga-As-Ga'-C(21')	-82.1(1)
Ga'-As-Ga-C(31)	84.0(2)	Ga-As-Ga'-C(31')	125.3(2)
Si(1)-As-Ga-Cl	-137.18(6)	Si(1')-As-Ga'-Cl	-89.57(5)
Si(1)-As-Ga-C(21)	117.6(2)	Si(1')-As-Ga'-C(21')	167.5(1)
Si(1)-As-Ga-C(31)	-32.5(2)	Si(1')-As-Ga'-C(31')	14.9(2)
Si(1')-As-Ga-Cl	96.49(6)	Si(1)-As-Ga'-Cl	143.04(5)
Si(1')-As-Ga-C(21)	-8.7(2)	Si(1)-As-Ga'-C(21')	40.1(1)
Si(1')-As-Ga-C(31)	-158.8(2)	Si(1)-As-Ga'-C(31')	-112.5(2)
As-Ga-Cl-Ga'	21.39(3)	As-Ga'-Cl-Ga	-21.40(3)
C(21)-Ga-Cl-Ga'	138.2(1)	C(21')-Ga'-Cl-Ga	88.7(2)
C(31)-Ga-Cl-Ga'	-90.8(1)	C(31')-Ga'-Cl-Ga	-140.2(2)

Compound 3

Ga(2)-As-Ga(1)-C(111)	-105.0(2)	Ga(1)-As-Ga(2)-C(211)	113.6(2)
Ga(2)-As-Ga(1)-As'	0.0(-)	Ga(1)-As-Ga(2)-As'	0.0(-)
Ga(2)-As-Ga(1)-C(111')	115.5(2)	Ga(1)-As-Ga(2)-C(211')	-106.0(2)
Si(1)-As-Ga(1)-C(111)	13.0(2)	Si(1)-As-Ga(2)-C(211)	-12.5(2)
Si(1)-As-Ga(1)-As'	118.0(1)	Si(1)-As-Ga(2)-As'	-126.0(1)
Si(1)-As-Ga(1)-C(111')	-126.5(2)	Si(1)-As-Ga(2)-C(211')	128.0(2)
Si(2)-As-Ga(1)-C(111)	135.1(2)	Si(2)-As-Ga(2)-C(211)	-130.7(2)
Si(2)-As-Ga(1)-As'	-119.9(1)	Si(2)-As-Ga(2)-As'	115.7(1)
Si(2)-As-Ga(1)-C(111')	-4.4(2)		

<sup>a</sup>The torsion angle A-B-C-D is defined as positive if, when viewed along the B-C bond, atom A must be rotated clockwise to eclipse atom D.

Table 6. Equations of Least-squares Planes through Groups of Atoms in 1 and 3 in the Form:  $PX + QY + RZ - S = 0$ ,<sup>a</sup> with, in Square Brackets, Displacements (Å) of Selected Atoms from these Planes

Compound 1

Plane 1A: As, Ga, Ga'

$$0.4900X + 0.8565Y - 0.1621Z - 4.5632 = 0$$

[As 0.000, Ga 0.000, Ga' 0.000, Cl 0.860,  
Si(1) -1.818, Si(1') 1.971, C(21) 1.420, C(21') -1.831,  
C(31) -1.812, C(31') 1.401]

Plane 1B Ga, Ga', Cl

$$0.6418X + 0.5361Y = 0.5484Z - 3.5139 = 0$$

[As 0.912, Ga 0.000, Ga' 0.000, Cl 0.000,  
Si(1) 0.091, Si(1') 3.248, C(21) 1.264, C(21') -1.918,  
C(31) -1.903, C(31') 1.213]

Dihedral angle between plane 1A and plane 1B = 30.40(6)°.

Compound 3

Plane 3A As, Ga(1), Ga(2), As'

$$-0.1221X + 0.0000Y - 0.9925Z + 4.6177 = 0$$

[As 0.000, Ga(1) 0.000, Ga(2) 0.000, As' 0.000,  
Si(1) 1.775, Si(2) -1.908, C(111) 1.733, C(211) 1.752]

Plane 3B As, Si(1), Si(2)

$$0.0363X + 0.9936Y - 0.1071Z - 3.4626 = 0$$

[As 0.000, Si(1) 0.000, Si(2) 0.000, Ga(1) 1.785,  
Ga(2) -1.942, As' -0.172, Si(1') -0.683, Si(2') 0.081]

Dihedral angle between plane 3A and plane 3B = 84.15(4)°.

<sup>a</sup>Cartesian coordinates ( $\underline{X}$ ,  $\underline{Y}$ ,  $\underline{Z}$ ) are related to the fractional atomic coordinates ( $\underline{x}$ ,  $\underline{y}$ ,  $\underline{z}$ ) by the following transformations:  $\underline{X} = \underline{x}a + \underline{z}c\cos\beta$ ,  $\underline{Y} = \underline{y}b$ ,  $\underline{Z} = \underline{z}c\sin\beta$ .

Table 7. Selected structural parameters for some compounds containing the  $\text{Ga-As-Ga-As}$  ring

Compound	Ga-As Bond length(s) (Å)	Ga-As-Ga Bond angle(s) (°)	As-Ga-As Bond angle(s) (°)	Ref
$[(\text{Me}_3\text{SiCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$ (3)	2.572(1) 2.561(1)	93.91(2)	85.85(3) 86.32(3)	this work
$\{\text{BrGa}[\text{As}(\text{CH}_2\text{SiMe}_3)_2]_2\}_2$	2.513(1) 2.521(1)	95.63(2)	84.37(2)	2
$[\text{Ga}[\text{As}(\text{CH}_2\text{SiMe}_3)_2]_3]_2$	2.581(1) 2.540(1) 2.559(1) 2.540(1)	96.02(4) 94.57(4)	83.58(4) 84.04	4
$[\text{Ph}_2\text{GaAs}(\text{CH}_2\text{SiMe}_3)_2]_2$	2.518(1) 2.530(1)	94.92(2)	85.08(2)	17
$(\text{Me}_2\text{GaAsBu}^t)_2$	2.541(1) 2.558(1)	95.69(2)	84.31	19

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